

CLAIMS

We Claim:

- 5 1. A method of molecular imprinting of polymer materials, comprising the steps of:
 - expanding a mixture containing a propellant and monomers to form particles;
 - introducing a template into said particles which is selectively releasable from a polymer formed from said monomers in said particles;
 - polymerizing said particles in the presence of said template to form composite particles having polymer and template, wherein said template is not bound to said polymer; and
 - extracting said template from said composite particles without distorting a morphology of said composite particles to provide polymerized particles imprinted by said template with a size and arrangement of chemical functional groups complementary to said template.
- 10 2. The method of claim 1 wherein said introducing step is performed by combining said template with said mixture prior to said expanding step.
- 15 3. The method of claim 2 wherein said propellant dissolves said monomers and said template to form a homogenous mixture.
- 20 4. The method of claim 1 wherein said introducing step is performed by combining said template with said mixture after said expanding step.
- 25 5. The method of claim 4 wherein combining is performed by diffusing said template from a gas phase into said particles.

6. The method of claim 1 wherein said mixture further comprises a photoinitiator.

7. The method of claim 1 wherein said mixture further comprises a crosslinking agent.

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8. The method of claim 1 wherein said polymerizing step is performed in an initial and a final polymerization,

wherein in said initial polymerization, said particles are subjected to energy selected from the group consisting of heat and radiant energy in an amount sufficient to 10 initiate polymerization of said monomers, and

wherein in said final polymerization, said particles are subjected to energy selected from the group consisting of heat and radiant energy in an amount sufficient to fully polymerize said monomers.

15 9. The method of claim 8 wherein said energy used in said initial polymerization and said final polymerization can be the same or different, and is selected from the group consisting of heat, ultraviolet, gamma, and infrared radiation.

10. The method of claim 9 wherein said energy used in said initial polymerization and 20 said final polymerization are both ultraviolet radiation.

11. The method of claim 8 wherein said expanding step creates said particles from said mixture in a gaseous environment, and wherein said initial polymerization is performed by subjecting said particles to said energy in said gaseous environment.

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12. The method of claim 11 wherein said gaseous environment is inert.

13. The method of claim 12 wherein said gaseous environment is nitrogen.
14. The method of claim 11 wherein said gaseous environment includes air.
- 5 15. The method of claim 11 wherein said final polymerization is performed by subjecting said composite particles to said energy after said composite particles are collected on a substrate.
- 10 16. The method of claim 1 wherein said polymerizing step is performed by subjecting said particles to an energy source selected from the group consisting of heat and radiant energy.
17. The method of claim 1 wherein said monomers have solid state reactivity.
- 15 18. The method of claim 17 wherein said monomers are selected from the group consisting of vinyl stearate, vinyl acetate, isoprene, vinyl octacecyl ether, methacrylic acid, trioxane, 2,5-distrylpyrazine, 2,2'-(2,2-p-phenylene-divinyl)-bis-pyridine, diethyl p-phenylenediacrylate, dimethyl p-phenylenediacrylate, diolefinic compounds and diacetylenes.
- 20 19. The method of claim 1 wherein said monomers are the same.
- 20 20. The method of claim 1 wherein said monomers include at least two different chemical moieties.
- 25 21. The method of claim 1 wherein said monomers are selected from the group consisting of include acrylic acids, acrylamides, vinylbenzoic acids, acrylamino-sulfonic

acids, amino-metacrylamides, vinylpyridines, vinylimidazoles, vinyl-iminodiacetic acids, etherketones, and etheretherketones.

22. The method of claim 1 wherein said propellant includes at least one compound

5 selected from the group consisting of chlorofluorocarbons, hydrofluorocarbons, alkanes, alkenes, noble gases, nitrogen, sulfur hexafluoride, fluorocarbons, nitrous oxide, hydrogen, ammonia, carbon monoxide and carbon dioxide.

23. The method of claim 1 wherein said template is a chemical compound having a

10 molecular weight ranging from 10 to 1,000,000.

24. The method of claim 1 wherein said template is a biological compound or substrate.

25. The method of claim 1 wherein the propellant includes as at least one component a

15 supercritical fluid.

26. The method of claim 25 wherein said supercritical fluid solubilizes said monomers in

said mixture.

20 27. The method of claim 1 wherein said particles formed in said expanding step are less than one micron in size.

28. The method of claim 1 wherein said particles formed in said expanding step are a liquid.

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29. The method of claim 1 wherein said particles formed in said expanding step are a solid.

30. The method of claim 1 wherein said template introduced in said introducing step does not covalently bond to said monomers.
- 5 31. A method for coating a substrate surface with particles, comprising the steps of:
expanding a mixture containing a propellant and monomers to form a particle stream;
depositing particles on a substrate surface by directing said particle stream at said substrate surface, said depositing step being performed in a manner whereby said particles retain a morphology developed from said expanding step; and
10 polymerizing said particles on said substrate surface, wherein said polymerizing step adheres said particles to said substrate surface.
32. The method of claim 31 wherein said depositing step includes the step of periodically moving said substrate surface in and out of said particle stream.
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33. The method of claim 31 wherein said polymerizing step is performed by exposing said particles to radiant energy.
- 20 34. The method of claim 31 wherein said polymerizing step is performed by exposing said particles to thermal energy.
35. The method of claim 31 further comprising the steps of:
introducing a template into said particles prior to said polymerizing step which
25 does not covalently bind to said monomers; and
extracting said template from said particles after said polymerizing step without
distorting a morphology of said particles to provide polymerized particles imprinted by

said template with a size and arrangement of chemical functional groups complementary to said template.

36. The method of claim 31 wherein said depositing step produces a layer of said
5 particles which does not exceed 1 micron thick.

37. A method for storing optical information, comprising the steps of:

forming a composition comprising particles formed from a monomer of solid state reactivity and a polymer matrix;

10 selectively exposing a portion of said particles to energy sufficient to polymerize said monomers of solid state reactivity in said portion; and

heating said particles at a temperature sufficient to cause particles not exposed in said selectively exposing step to diffuse into said polymer matrix.

15 38. The method of claim 37 wherein said polymer matrix is selected from the group consisting of polycarbonates, polysiloxanes, and polyesters.

39. The method of claim 37 wherein said selectively exposing step polymerizes particles in a manner which creates a two dimensional image.

20 40. The method of claim 37 wherein said selectively exposing step polymerizes particles in a manner which creates a three dimensional image.

25 41. The method of claim 37 wherein said monomers of solid state reactivity are selected from the group consisting of vinyl stearate, vinyl acetate, isoprene, vinyl octacecyl ether, methacrylic acid, trioxane, 2,5-distrylpyrazine, 2,2'-(2,2-p-phenylene-

divinyl)-bis-pyridine, diethyl p-phenylenediacrylate, dimethyl p-phenylenediacrylate, diolephenic compounds and diacetylenes.

42. The method of claim 37 wherein said forming step includes the step of expanding a
5 mixture containing a propellant and said monomers of solid state reactivity into said polymer matrix.

43. A polymeric material with a molecular imprint made by a process comprising the steps of:

10 expanding a mixture containing a propellant and monomers to form particles;
introducing a template into said particles which does not covalently bind to said monomers;
polymerizing said particles in the presence of said template to form composite particles having polymer and template, wherein said template is not bound to said
15 polymer; and
extracting said template from said composite particles without distorting a morphology of said composite particles to provide polymerized particles imprinted by said template with a size and arrangement of chemical functional groups complementary to said template.

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44. The polymeric material of claim 43 wherein said composite particles are 50 microns or less in size.

45. The polymeric material of claim 43 wherein said composite particles are 1 micron or
25 less in size.

46. A device for selectively joining with an analyte in a sample, comprising:

a substrate; and

a plurality of polymeric particles imprinted by a template specific for said analyte adhered directly to a surface of said substrate by a chemical or mechanical bond with said polymeric particles.

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47. The device of claim 46 wherein said substrate is part of a sensor.

48. The device of claim 46 wherein said substrate is part of a chromatography device.

10 49. The device of claim 46 wherein said substrate is a conductive material.

50. The device of claim 46 wherein said substrate is an insulative material.

51. A filter, purifier, or separation device, comprising

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a porous substrate; and

a plurality of polymeric particles imprinted by a template specific for an analyte adhered to surfaces of said substrate by a chemical or mechanical bond with said polymeric particles.

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52. The filter of claim 51 wherein at least some of said surfaces to which said polymeric particles are adhered to are internal to said porous substrate.

53. A chemical delivery material, comprising:

25 a polymeric particle imprinted by a template specific for an analyte; and
an agent associated with said polymeric particle which is selectively releasable from said polymeric particle.

54. The chemical delivery material as recited in claim 1 wherein said agent is a drug.
55. The chemical delivery material as recited in claim 53 wherein said agent is releasable
5 by hydrolyzing bonds between said polymeric particle and said agent.
56. The chemical delivery material as recited in claim 53 wherein said polymeric particle
is biodegradable.
- 10 57. The chemical delivery material as recited in claim 53 wherein said agent is an
enzyme.
58. The chemical delivery material as recited in claim 53 wherein said agent includes a
nucleic acid sequence.
- 15 59. The chemical delivery material as recited in claim 53 wherein said agent is a protein.
60. The chemical delivery material as recited in claim 53 wherein said agent is a vitamin.
- 20 61. A method for preparing a material for selectively joining with an analyte, comprising
the steps of:
expanding a mixture containing a propellant and monomers to form particles;
introducing a template into said particles which is selectively releasable from a
polymer formed from said monomers in said mixture and wherein said template is
25 different from said analyte;

polymerizing said particles in the presence of said template to form composite particles having polymer and template; and

extracting said template from said composite particles without distorting a morphology of said composite particles to provide polymerized particles imprinted by
5 said template.

62. A non-agglomerated, solvent free collection of a plurality of selectively polymerizable particles, each of which are comprised of a monomer of solid state reactivity, and each of which is 1 micron or smaller in size.

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63. The non-agglomerated, solvent free collection recited in claim 62 wherein at least to of said plurality of particles are comprised different monomer materials.

15 64. The non-agglomerated, solvent free collection recited in claim 62 wherein at least one of the monomeric particles in said plurality is molecularly imprinted.

65. A collection of selectively polymerizable particles, consisting of:

a plurality of monomeric particles each of which is composed of a monomer of solid state reactivity, and each of which is one micron or smaller in size.

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66. A coated substrate, comprised of:

a substrate;

a plurality of monomer containing particles of solid state reactivity positioned on said substrate, each of said monomer containing particles being 100 microns or smaller in
25 size.

67. The coated substrate of claim 66 wherein said plurality of monomeric particles cover only a patterned portion of a surface of said substrate.
68. The coated substrate of claim 66 wherein at least two of said monomer containing particles are composed of different materials.
- 5 69. The coated substrate of claim 66 wherein at least one of said monomer containing particles contains a template for molecularly imprinting positioned therein.
- 10 70. The coated substrate of claim 66 wherein said coated particles are one micron or less in size.
71. A method of molecular imprinting of particles, comprising the steps of:
expanding a mixture containing a propellant and at least one compound which can conform to a molecular configuration of a template to create particles;
- 15 introducing a template into said particles which is selectively releasable from said compound in said particles;
- solidifying said compound in said particles with said template positioned therein;
and
- 20 extracting said template from said particles without distorting a morphology of said particles to provide molecularly imprinted particles.
72. The method of claim 71 wherein said compound is a polymer.
- 25 73. The method of claim 71 wherein said compound is a monomer.

74. The method of claim 71 wherein said compound is a biological substance.

75. The method of claim 71 wherein said solidifying step is performed by exposing said particles to a sufficient amount of energy so as to solidify said compound in said
5 particles.

76. A method for coating a substrate with a thin coating, comprising the steps of:

solubilizing a solute with propellant containing at least one supercritical fluid;
expanding a mixture of said propellant and solute to form a particle stream;
10 depositing particles from said particle stream on a substrate surface by directing
said particle stream at substrate surface from an offset position.

77. The method for coating recited in claim 76, wherein said offset position ranges from
0.5 to 5.0 cm.

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78. The method for coating recited in claim 76 wherein said particles are liquid.

79. The method for coating recited in claim 76 wherein said particles are solid.

20 80. The method for coating recited in claim 76 wherein the concentration of solute in
said mixture of propellant and solute is 1 wt% or less.

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